

ARTICLE PRINCIPAL

Recouvrant en partie

LA THÈSE DE DOCTORAT ÈS SCIENCES PHYSIQUES

présentée

A LA FACULTÉ DES SCIENCES

DE PARIS

par

Georges ROUSSI

pour obtenir

LE GRADE DE DOCTEUR ÈS-SCIENCES

Sujet de la Thèse :

Contribution à l'étude des organomagnésiens allyliques.

Structure et stéréochimie des produits obtenus avec les époxydes, les aldéhydes, les nitriles et les alcools allyliques.

soutenue le 17 décembre 1969 devant la Commission d'examen

Mlle J. FICINI

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ADDITION OF GRIGNARD REAGENTS TO THE DOUBLE BOND OF
ALLYLIC ALCOHOLS

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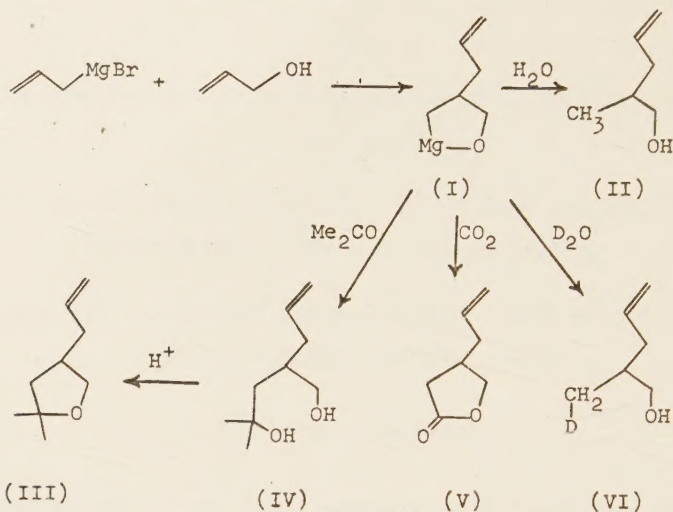
We have found that reactive (e.g., allyl and benzyl) Grignard reagents add to the double bond of allyl alcohol.

Our first indication of this reaction was the observation that allyl magnesium bromide, after being prepared in the usual way and allowed to stand under what was thought to be (but obviously was not) pure nitrogen, afforded upon hydrolysis 2-methyl- Δ^4 -pentenol (II) [identified by comparison with an authentic sample (1) prepared from malonic ester].

Further investigation showed that the yield of this alcohol (II) was both better (50%) and more reproducible when a solution of allyl magnesium bromide (2.5 mols.) in ether was boiled with allyl alcohol for 50 hours and then hydrolysed.

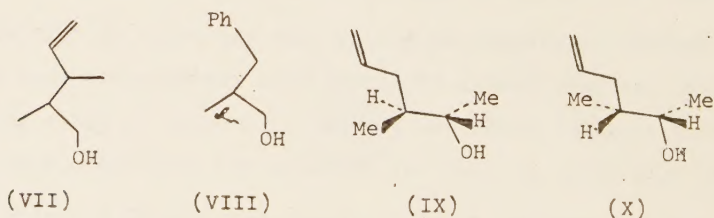
The intermediate formed before hydrolysis is probably the adduct (I) (2), which is itself a Grignard reagent; addition of deuterium oxide to this intermediate afforded the deuterated alcohol (VI), carbon dioxide the γ -lactone (V), and acetone

the 1-4 diol (IV), which was readily converted into the tetra-



hydrofuran (III) (3).

In a similar fashion, "butenyl" magnesium bromide and allyl alcohol, refluxed for 8 hours in ether, afforded, in 30% yield, the alcohol (VII), apparently as a mixture of diastereoisomers. The reaction with benzyl magnesium chloride was much slower, and refluxing for 170 hours in benzene was required to



obtain a 10% yield of 2-benzylpropanol (VIII).

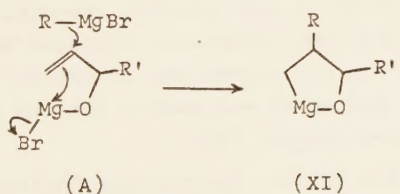
Alkyl substitution on the double bond of the allylic alco-

hol is an unfavourable structural feature; crotyl alcohol and β -methallyl alcohol gave <5% of addition products with allyl magnesium bromide after refluxing for 170 hours in ether.

α -Methallyl alcohol, however, afforded, in 16% yield, an 8:1 mixture of erythro (IX) and threo (X) 3-methyl- Δ^5 -2-hexenol [identified by comparison with authentic samples (4)].

It seems unlikely that these reactions are due to Ziegler type catalysis by transition-metal impurities in the "Grignard grade" magnesium used to prepare the reagents, since the reaction between allyl alcohol and allyl magnesium bromide was only very slightly slower when "nuclear grade" magnesium was used; moreover, little (if any) oligomerisation was observed even when a large excess of allyl magnesium bromide was present.

The neighbouring magnesium alkoxide group therefore probably plays an important rôle, which could be that of an intramo-



lecular electrophile (cf. A). This would be consistent with the stereochemistry of the reaction in the α -methallyl alcohol case, since the predominant diastereoisomer (IX) has the same configuration as the cyclic adduct (XI; R = allyl, R' = Me) in which R and R' are trans; it would also be consistent with the fact that the reaction is faster in refluxing ether than in refluxing tetrahydrofuran, and faster with allyl magnesium bromide than

with diallyl magnesium.

Although Grignard reagents are not generally considered to be capable of uncatalysed 1-2 addition to carbon-carbon double bonds, a few such reactions have, in fact, already been reported (5, 6); organo-lithium reagents (6, 7) and lithium aluminium hydride (8) are also known to add in this fashion. These 1-2 additions all have in common the fact that they are facilitated by the presence of a neighbouring electronegative substituent (9).

References

1. G.I.Fray and N.Polgar, J.Chem.Soc., 2036 (1956).
2. A non cyclic structure containing two magnesium atoms per molecule is, of course, also a possibility.
3. Compounds (II-VIII) had spectral properties (IR and nmr) consistent with the structures assigned to them. We are indebted to Drs A.Gaudemer and J.Parello for help with the nmr spectra and to Mr H.E.Audier for the mass spectrum of the deuterated alcohol (VI).
4. H.Felkin and G.Roussi, Tetrahedron Letters, 4153 (1965).
5. M.S.Kharasch and O.Reinmuth, "The Grignard Reactions of Non-metallic Substances", Constable, London, p.87 (1954). For a very recent example involving allyl magnesium bromide and a homoallylic alcohol, see J.J.Eisch and G.R.Husk, J.Amer.Chem.Soc., 87, 4194 (1965).
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8. N.G.Gaylord, "Reduction with Complex Metal Hydrides", Interscience, New York, p.925 (1956).
9. We are indebted to Prof. M.Fétizon for stimulating discussions, and to the Petroleum Research Fund of the American Chemical Society for partial support of this work.



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